

## Final Report

### Early Transition Metal Oxides as Catalysts: Crossing Scales from Clusters to Single Crystals to Functioning Materials

#### Oxide Clusters – Electronic Structure and Chemical Bonding

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#### Abstract

The overall goal of this program is to investigate the electronic structure and chemical bonding of early transition metal oxide clusters and use them as well-defined molecular models to obtain insight into properties and mechanisms of oxide catalysts, as well as to provide accurate spectroscopic and molecular information to verify theoretical methods used to predict materials properties. A laser vaporization cluster source is used to produce metal oxide clusters with different sizes, structures, and compositions. Well-defined inorganic polyoxometalate clusters in solution are transported in the gas phase using electrospray. Two state-of-the-art photoelectron spectroscopy apparatuses are used to interrogate the oxide clusters and polyoxometalate anions in the gas phase to obtain spectroscopic and electronic structure information. The experimental effort is assisted by theoretical calculations to understanding the structures, chemical bonding, and catalytical properties of the transition metal oxide clusters. The research approach combines novel and flexible experimental techniques and advanced theoretical/computational methodologies and seeks molecular-level information to aiding the design of new catalysts, as well as mechanistic understanding.

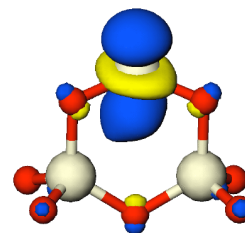
We have focused on the investigation of tungsten oxide clusters containing three W atoms:  $W_3O_x^-$  ( $x = 7-11$ ). A number of interesting findings have been made. We observed that the oxygen-poor  $W_3O_8$  cluster contains a localized  $W^{4+}$  center, which can be used as a molecular model for O-deficient defect sites. A chemisorption energy was obtained through density functional calculations for  $W_3O_8 + O_2 \rightarrow W_3O_{10}$  as -78 kcal/mol. We further found that the neutral stoichiometric  $W_2O_6$  and  $W_3O_9$  clusters do not react with  $O_2$  and they only form physisorbed complexes,  $W_2O_6(O_2)$  and  $W_3O_9(O_2)$ . However, the negatively charged  $W_2O_6^-$  and  $W_3O_9^-$  clusters are found to form chemisorbed complexes due to the presence of the extra electron. Thus, the  $W_2O_6^-$  and  $W_3O_9^-$  negative clusters can be viewed as models for  $O_2$  interaction with a reduced W site ( $W^{5+}$ ) on the oxide surface. These studies also led to the surprising observation of the first d-orbital aromatic clusters in  $W_3O_9^{2-}$  and  $Mo_3O_9^{2-}$ , which each contains a completely delocalized three-center two-electron bond made entirely made of the metal d orbitals. This last result was highlighted in both *Chem & Eng. News* and *Nature*.

We further studied a series of small metalate anions using electrospray, including the hydroxo and methoxo oxometalate  $MO_3(OH)^-$  and  $MO_3(OCH_3)^-$ , and the dimetalates:  $M_2O_7^{2-}$ ,  $MM'O_7^{2-}$ , and  $M_2O_7^-$  (M, M' = Cr, Mo, and W).

#### Description of Results

**On the structure and chemical bonding of tri-tungsten oxide clusters  $W_3O_n^-$  and  $W_3O_n$  ( $n = 7-10$ ):  $W_3O_8$  as a molecular model for O-deficient defect sites in tungsten oxides.** Electronic and structural properties of a series of tri-tungsten oxide clusters,  $W_3O_n^-$  and  $W_3O_n$  ( $n = 7-10$ ), were investigated using

photoelectron spectroscopy and density functional theory (DFT) calculations. Both W 5d and O 2p detachment features were observed for  $n = 7-9$ , whereas only detachment features from O 2p type orbitals were observed for  $W_3O_{10}^-$  at extremely high electron binding energies ( $>7$  eV). A large HOMO-LUMO gap ( $\sim 3.4$  eV) was observed for the stoichiometric  $W_3O_9$  cluster, which already reaches the bulk value, suggesting that  $W_3O_9$  can be viewed as the smallest molecular model for bulk  $WO_3$ . Extensive DFT calculations were carried out to locate the most stable structures for both the anion and neutral clusters; time-dependent DFT method is used to predict the vertical detachment energies and to compare with the experimental data. It was shown that  $W_3O_9$  possesses a  $D_{3h}$  structure, in which each W atom is tetrahedrally coordinated with two bridging O atoms and two terminal O atoms.  $W_3O_8$  and  $W_3O_7$  can be viewed as removing one and two terminal O atoms from  $W_3O_9$ , respectively, whereas  $W_3O_{10}$  can be viewed as replacing a terminal O in  $W_3O_9$  by a peroxo  $O_2$  unit. We showed that  $W_3O_8$  contains a localized  $W^{4+}$  site (Fig. 1), which can readily react with  $O_2$  to form the  $W_3O_{10}$  clusters with a calculated  $O_2$  adsorption energy of  $-78$  kcal/mol. It is suggested that the  $W_3O_8$  cluster can be viewed as a molecular model for O-deficient site in tungsten oxides.



HOMO (31a')<sup>2</sup>

Fig. 1. The localized HOMO in  $W_3O_8$ .

**Experimental and theoretical characterization of superoxide complexes  $W_2O_6(O_2^-)$  and  $W_3O_9(O_2^-)$ : models for the interaction of  $O_2$  with reduced W sites on tungsten oxide surfaces.** Two O-rich tungsten oxide clusters,  $W_2O_8^-$  and  $W_3O_{11}^-$ , were produced and investigated. The two anions were best considered as  $W_2O_6(O_2^-)$  and  $W_3O_9(O_2^-)$ , respectively, each containing a side-on bound superoxide ligand, whereas the neutral clusters  $W_2O_8$  and  $W_3O_{11}$  were shown to involve  $O_2$  physisorbed to the  $W_2O_6$  or  $W_3O_9$  stoichiometric cluster. This study indicates that the extra electron in  $W_2O_6^-$  and  $W_3O_9^-$  are capable of activating dioxygen by non-dissociative electron transfer ( $W\ 5d \rightarrow O_2\ \pi^*$ ), and the two anionic clusters can be viewed as models for reduced defect sites on tungsten oxide surfaces for the chemisorption of  $O_2$ .

**Observation of d-orbital aromaticity.** Aromatic molecules are usually planar species formed by main group elements, whose bonding is primarily from the s or p orbitals. We found experimental and theoretical evidence for aromaticity from d-orbitals during our investigation of tungsten oxide clusters.  $W_3O_9$  and  $Mo_3O_9$  were both shown to possess a  $D_{3h}$  structure with a low-lying unoccupied molecular orbital formed from the metal d orbitals. Occupation of this orbital by one or two electrons gives rise to strong three-center one-electron and three-center two-electron metal-metal bonds (Fig. 2), respectively, significantly reducing the M-M distances in  $M_3O_9^-$  and  $M_3O_9^{2-}$ . The totally delocalized three-center bond (Fig. 2) renders aromaticity for both  $M_3O_9^-$  and  $M_3O_9^{2-}$ , further evidenced by a large calculated resonance energy. The  $M_3O_9^-$  and  $M_3O_9^{2-}$  species are highly stable and represent a new class of d-orbital aromatic molecules.

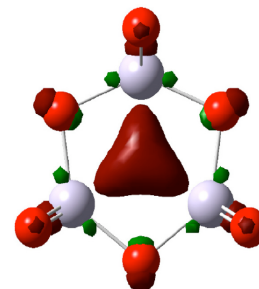


Fig. 2. The three-center bond in  $W_3O_9^{2-}$ .

**Electronic structure of the hydroxo and methoxo oxometalate anions  $MO_3(OH)^-$  and  $MO_3(OCH_3)^-$  ( $M = Cr, Mo$  and  $W$ ).** The electronic structure of the mononuclear hydroxo  $MO_3(OH)^-$  and methoxo  $MO_3(OCH_3)^-$  Group 6 oxometalate anions ( $M = Cr, Mo$  and  $W$ ) were examined by photoelectron spectroscopy and electronic structure calculations at the density functional and CCSD(T) levels of theory. All of the anions exhibited high electron binding energies ( $> 4.9$  eV), with the lowest energy detachment features arising from oxygen 2p based orbitals. The combined experimental and theoretical results allowed the change in molecular orbital energy levels to be investigated as a function of metal ( $Cr, Mo$  or  $W$ ) and ligand ( $-OH, -OCH_3$ ). A number of fundamental thermodynamic properties of the anions and corresponding neutrals were predicted based on the theoretical calculations. The calculations indicate high O-H bond dissociation energies for  $MO_2(OR)(O-H)$  ( $R = H, CH_3$ ) and  $MO_3(O-H)$ , consistent with their high Bronsted acidities (just below that of  $H_2SO_4$  in the gas phase) and the high ionization energies of their conjugate base anions. This suggests the corresponding radicals should readily abstract H atoms from organic molecules.

**Photoelectron spectroscopy of doubly and singly charged group VIB dimetalate anions:  $M_2O_7^{2-}$ ,  $MM'O_7^{2-}$ , and  $M_2O_7^-$  ( $M, M' = Cr, Mo, W$ ).** We produced both doubly and singly charged Group

VIB dimetalate species,  $M_2O_7^{2-}$ ,  $MM'O_7^{2-}$ , and  $M_2O_7^-$  ( $M, M' = Cr, Mo, W$ ) using two different experimental techniques (electrospray for the doubly charged anions and laser vaporization for the singly charged anions) and investigated their electronic and geometric structures. Distinct changes in the electronic and geometric structures as a function of the metal and charge state were observed. The electron binding energies of the heteronuclear dianions  $MM'O_7^{2-}$  were observed to be roughly the average of those of their homonuclear counterparts,  $M_2O_7^{2-}$  and  $M'_2O_7^{2-}$ . Density functional calculations indicated that  $W_2O_7^{2-}$ ,  $W_2O_7^-$ , and  $W_2O_7$  possess different ground state structures: the dianion is highly symmetric ( $D_{3d}, ^1A_{1g}$ ) with a single bridging oxo ligand, the monoanion is a doublet ( $C_{2v}, ^2A$ ) with two bridging oxo ligands and a radical terminal oxo ligand, while the neutral is a singlet ( $C_{2v}, ^1A$ ) with two bridging oxo ligands and a terminal peroxo ligand. The combined experimental and theoretical study provides insights into the evolution of geometric and electronic structures as a function of charge state. The clusters identified might provide insights into the possible structures of reactive species present in early transition-metal oxide catalysts that are relevant to their reactivity and catalytic function.

## Publications

1. "Electronic Structure and Chemical Bonding in  $MO_n^-$  and  $MO_n$  Clusters ( $M = Mo, W; n = 3-5$ ): A Photoelectron Spectroscopy and ab Initio Study" (H. J. Zhai, B. Kiran, L. F. Cui, X. Li, D. A. Dixon, and L. S. Wang), *J. Am. Chem. Soc.* **126**, 16134-16141 (2004).
2. "Photoelectron Spectroscopy of Free Polyoxoanions  $Mo_6O_{19}^{2-}$  and  $W_6O_{19}^{2-}$  in the Gas Phase" (X. Yang, T. Waters, X. B. Wang, R. A. J. O'Hair, A. G. Wedd, D. A. Dixon, J. Li, and L. S. Wang), *J. Phys. Chem. A* **108**, 10089-10093 (2004).
3. "Electronic and Structural Evolution and Chemical Bonding in Ditungsten Oxide Clusters:  $W_2O_n^-$  and  $W_2O_n$  ( $n = 1-6$ )" (H. J. Zhai, X. Huang, L. F. Cui, X. Li, J. Li, and L. S. Wang), *J. Phys. Chem. A* **109**, 6019-6030 (2005).
4. "Observation of d-Orbital Aromaticity" (X. Huang, H. J. Zhai, B. Kiran, and L. S. Wang), *Angew. Chem. Int. Ed.* **44**, 7251-7254 (2005). *Angew. Chem.* **117**, 7417-7420 (2005). (**Science Concentrate: C&E News** **83** (**43**), October 24, 2005, page 48; **Research Highlight: Nature** **438**, November 17, 2005, page 261)
5. "Photoelectron Spectroscopy of Doubly and Singly Charged Group VIB Dimetalate Anions:  $M_2O_7^{2-}$ ,  $MM'O_7^{2-}$ , and  $M_2O_7^-$  ( $M, M' = Cr, Mo, W$ )" (H. J. Zhai, X. Huang, T. Waters, X. B. Wang, R. A. J. O'Hair, A. G. Wedd, and L. S. Wang), *J. Phys. Chem. A* **109**, 10512-10520 (2005).
6. "Electronic Structure of the Hydroxo and Methoxo Oxometalate Anions  $MO_3(OH)^-$  and  $MO_3(OCH_3)^-$  ( $M = Cr, Mo$  and  $W$ )" (T. Waters, X. B. Wang, S. G. Li, B. Kiran, D. A. Dixon, and L. S. Wang), *J. Phys. Chem. A* **109**, 11771-11780 (2005).
7. "On the Structure and Chemical Bonding of Tri-Tungsten Oxide Clusters  $W_3O_n^-$  and  $W_3O_n$  ( $n = 7-10$ ):  $W_3O_8$  As A Molecular Model for O-Deficient Defect Sites in Tungsten Oxides" (X. Huang, H. J. Zhai, J. Li, and L. S. Wang), *J. Phys. Chem. A* **110**, 85-92 (2006).
8. "Experimental and Theoretical Characterization of Superoxide Complexes  $W_2O_6(O_2^-)$  and  $W_3O_9(O_2^-)$ : Models for the Interaction of  $O_2$  with Reduced W Sites on Tungsten Oxide Surfaces" (X. Huang, H. J. Zhai, T. Waters, J. Li, and L. S. Wang), *Angew. Chem. Int. Ed.* **45**, 657-660 (2006).
9. "Formation of Monodisperse  $(WO_3)_3$  Clusters on  $TiO_2(110)$ " (O. Bondarchuk, X. Huang, J. Kim, B. D. Kay, L. S. Wang, J. M. White, and Z. Dohnálek), *Angew. Chem. Int. Ed.* **45**, 4786-4789 (2006); *Angew. Chem.* **118**, 4904-4907 (2006).
10. "Photoelectron Spectroscopy of Free Multiply Charged Keggin Anions  $\alpha-[PM_{12}O_{40}]^{3-}$  ( $M = Mo, W$ ) in the Gas Phase" (T. Waters, X. Huang, X. B. Wang, H. K. Woo, R. A. J. O'Hair, A. G. Wedd, and L. S. Wang), *J. Phys. Chem. A* **110**, 10737-10741 (2006).
11. "Probing the Electronic Properties of Dichromium Oxide Clusters  $Cr_2O_n^-$  ( $n = 1-7$ ) Using Photoelectron Spectroscopy" (H. J. Zhai and L. S. Wang), *J. Chem. Phys.* **125**, 164315-1-9 (2006).

12. "Probing the Electronic Structure and Band Gap Evolution of Titanium Oxide Clusters  $(\text{TiO}_2)_n^-$  ( $n = 1-10$ ) Using Photoelectron Spectroscopy" (H. J. Zhai and L. S. Wang), *J. Am. Chem. Soc.* **129**, 3022-3026 (2007).

#### **Special Recognitions Received by PI**

1. Named 2005 John Simon Guggenheim Fellow.
  2. Distinguished Faculty Award, College of Sciences, Washington State University
  3. 2006 Humboldt Senior Research Award
  4. 2007 Sahlin Faculty Excellence Award for Research, Scholarship & Arts, Washington State University
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